Ising Model of a Glass Transition

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Numerical simulations indicate that several different glass transitions, for polydisperse systems in both two and three dimensions, are characterized by diverging correlation lengths. These correlations are described by Ising-like critical exponents, and are associated with diverging, Vogel-Fulcher-Tamann, structural relaxation times. Related simulations of thermalized hard-disks indicate that the curves of pressure versus packing fraction for different polydispersities exhibit a sequence of transition points, starting with a liquid-hexatic transition for the monodisperse case, and crossing over with increasing polydispersity to glassy, Ising-like critical points. I propose to explain these observations by assuming that glass-forming materials contain twofold degenerate, topologically ordered clusters of particles, similar to the two-state systems that have been invoked to explain other glassy phenomena. This paper starts with a brief statistical derivation of the thermodynamics of thermalized, hard-core particles. It then discusses how a two-state, Ising-like model can be described within that framework in terms of a small number of statistically relevant, internal state variables. The resulting theory is remarkably consistent with the simulation data, but fails near the transition points where Ising symmetry must cross over to rotational symmetry. I also suggest a possible relation between Ising correlation lengths and the Vogel-Fulcher-Tamann formula.

I. INTRODUCTION

Among the deepest outstanding questions in materials theory is whether glass forming systems undergo truly thermodynamic phase transitions, and whether, if so, those transitions are characterized by diverging length scales. I argue here that recent numerical simulations, especially those by Tanaka and coworkers [1, 2], imply that this thermodynamic picture is correct; and I propose an Ising-like scenario within which glassy phase transitions and critical correlation lengths may be understood.

Many current theories of amorphous materials assume that glassy slowing down is fundamentally a kinetic phenomenon that may, or may not, culminate at a sharply defined temperature or density. For example, facilitated kinetic Ising models have no nontrivial thermodynamic properties.[3] Similarly, the random first-order transition theory (RFOT) [4, 5] starts by computing a thermally activated relaxation rate that implies a diverging length scale. My own excitation-chain (XC) theory [6] originally was introduced as a way of avoiding the weaknesses I perceived in RFOT [7]; but the XC theory uses an analogous, intrinsically dynamic strategy, and produces a similarly diverging length scale (with apparently incorrect critical exponents). If glassy systems do, in fact, undergo thermodynamic phase transitions, then that equilibrium behavior ought to be the basis for a theory of relaxation rates, and not the other way around. Theories of relaxation mechanisms ought to start with a theory of the equilibrium state – if such a theory exists.

The strongest evidence in favor of glassy, thermodynamic phase transitions is the recent discovery that several different glassy systems exhibit growing bond-orientational order, with correlation lengths that diverge at critical temperatures or packing fractions. In [1], Tanaka and coworkers describe molecular dynamics simulations of a variety of two and three dimensional systems, including polydisperse hard disks and spheres. A related analysis by Mosayebi et al [8], for a three dimensional, bidisperse, Lennard-Jones system, produces results that are consistent with those of [1], and provides additional mathematical rigor and physical insight. This length scale may be the same as the one deduced indirectly in numerical simulations by Karmakar et al. [9].

The picture that emerges in [1] and [8] is that the diverging, equilibrium correlation lengths ξ are described by Ising-like critical exponents. Specifically, ξ is proportional to $t^{-\nu}$ with $\nu \cong 2/d$, where d is the spatial dimensionality, and t is a dimensionless measure of the distance from a critical point. For thermally controlled systems, $t = (T - T_c)/T_c$, where T_c is the critical temperature. For hard-core particles, the temperature T is replaced by the inverse of the packing fraction ϕ. For both $d = 2$ and 3, the structural relaxation time τ_α is found to be consistent with a Vogel-Fulcher-Tamann (VFT) relation, $\log(\tau_\alpha) \sim t^{-1}$, which may be further evidence of Ising-like universality.

More evidence bearing on the existence of glassy phase transitions is summarized in Fig. 2 of [2], where Kawasaki and Tanaka have plotted the pressure p as a function of ϕ for simulated hard disks at a sequence of increasing percentage polydispersities Δ. As expected, the monodisperse system at $\Delta = 0\%$ exhibits an apparently sharp transition between liquid and hexatic phases at $\phi \cong 0.69$. With increasing Δ, the transition points on the $p(\phi)$ curves move to larger p's and ϕ's, and become less and less distinct. They are invisible in the pressure data above $\Delta = 9\%$, which is the value of the polydispersity for which Tanaka et al. [1] report a bond-orientational correlation length that extrapolates to infinity at $\phi \cong 0.787$. The important point for present purposes is that the sequence of pressure curves in Fig. 2 of [2] appears to indicate a smooth crossover from a liquid-hexatic transition at $\Delta = 0\%$ to Ising-like critical points

for $\Delta \geq 9\,\%$ – a qualitative change of universality class.

In thermodynamic equilibrium, hard-core systems are characterized entirely by steric constraints and configurational entropy. They are the antitheses of the solvable models of systems with infinitely long-ranged interactions that sometimes are used as starting points for glass theories, e.g. RFOT. In hard-core systems, there is no stored elastic energy, and therefore there can be no such thing as the vibrational entropy sometimes postulated to be responsible for crystalline ordering in such materials. Nor, for classical systems of this kind, can the entropy associated with kinetic degrees of freedom play any role in determining equilibrium structures; the kinetic energy simply factors out of the partition function. Thus, hard-core simulations, and analogous experiments using hard-core colloidal particles, present a particularly clean theoretical challenge. In this paper, I consider only such systems. Accordingly, in Sec. II, I present a brief statistical derivation of the thermodynamics of thermalized, hard-core particles, which also serves to emphasize the role of properly chosen internal state variables.

In the main part of this paper, I use this thermodynamic framework to develop an Ising-like model of disordered, hard-core materials. The basic ingredient of this model is a population of twofold degenerate, topologically oriented, clusters of particles, similar to the two-state systems that have been invoked to explain other glassy phenomena.[10, 11] In Sec. III, I propose a rationale for this model, and then, in Secs. IV and V, show that it predicts both Ising-like, bond-orientational correlations, and a sequence of critical ordering transitions along the $p(\phi)$ curves. In Sec. VI, I suggest a possible relation between the Ising correlation lengths and the observed Vogel-Fulcher-Tamann behavior of the structural relaxation rates, thus tentatively adding support for the two-state hypothesis.

In Sec. III, however, I also argue that Ising symmetry must cross over to full rotational symmetry when the correlations become sufficiently long-ranged near critical points. As a result, the two-state theory must fail in the immediate vicinities of ordering transitions. Nevertheless, this theory accounts remarkably well for the simulation results, and may therefore provide a unified point of view for understanding a wide range of glassy behaviors. I conclude in Sec. VII with some remarks about that conjecture.

II. STATISTICAL THERMODYNAMICS

In preparation for developing a model of thermalized, hard-core, glass forming particles, we need to understand the statistical thermodynamics of such systems. The following analysis is based on [12] and is almost, but not exactly, identical to that presented in [13].

In the absence of interaction energies, the only extensive quantity available for describing a hard-core system is its volume V. (Throughout this paper, the term "volume" means either three dimensional volume or two dimensional area.) V must be a function of the entropy S plus a small set of internal state variables that govern the responses of the system to external forces. Denote these variables by $\Lambda_\alpha, \quad \alpha = 1, \ldots n$ or, equivalently, by the set $\{\Lambda\}$. As discussed in [12], the Λ_α must be extensive quantities, or spatial averages of such quantities, each carrying its own entropy. In the thermodynamic limit of very large systems, the total entropy, say $S(V, \{\Lambda\})$, must approach its equilibrium value when the Λ_α approach their own equilibrium values. I discuss the choice of these variables in Section IV; but, first, I consider only the general structure of the theory.

For simplicity, assume that the kinetic degrees of freedom of the particles plus the degrees of freedom of the heat bath in which the system is immersed constitute a single thermal reservoir at temperature $\theta = k_B T$. Denote the energy of this reservoir by U_R. Because the hard-core configurational degrees of freedom carry no potential energy, U_R is the total energy of the system. Therefore, the first law of thermodynamics is simply $\dot{U}_R = -p\,\dot{V}$.

The total entropy of this system, $S(V, \{\Lambda\})$, is the sum of the configurational entropy, say S_C, and the entropy of the reservoir, say S_R. $S_C(V, \{\Lambda\})$ is a constrained entropy computed by counting the number of configurations with fixed values of V and $\{\Lambda\}$. Conversely, $V = V(S_C, \{\Lambda\})$. In analogy to the notation of Edwards and coworkers [14–16], define the compactivity X by writing

$$X = \left(\frac{\partial V}{\partial S_C}\right)_{\{\Lambda\}}. \qquad (2.1)$$

Thus, the first law becomes

$$\dot{U}_R = \theta\,\dot{S}_R = -p\,\dot{V}$$

$$= -p\,X\,\dot{S}_C - p\sum_{\alpha=1}^{n}\frac{\partial V}{\partial \Lambda_\alpha}\dot{\Lambda}_\alpha. \qquad (2.2)$$

The second law, $\dot{S}_C + \dot{S}_R \geq 0$, is best written by using Eq.(2.2) to eliminate $\dot{S}_C$, with the result

$$\dot{S}_R\left(1 - \frac{\theta}{p\,X}\right) - \frac{1}{X}\sum_{\alpha=1}^{n}\frac{\partial V}{\partial \Lambda_\alpha}\dot{\Lambda}_\alpha \geq 0. \qquad (2.3)$$

As usual, the requirement that this inequality be satisfied for arbitrary variations of external conditions implies that each of the terms on the right-hand side of Eq.(2.3) be separately non-negative. In particular, the first term is non-negative if

$$\dot{S}_R \propto 1 - \frac{\theta}{p\,X}, \qquad (2.4)$$

which means that, in the equilibrium limit, $X \to \theta/p$.

To interpret the remaining terms on the right-hand side of Eq.(2.3), remember that, in a statistical sense,

the internal variables $\{\Lambda\}$ describe only a fraction of the number of configurational degrees of freedom of the system. To account for the remaining internal degrees of freedom, write

$$S_C(V, \{\Lambda\}) = \mathcal{S}(\{\Lambda\}) + S_1, \qquad (2.5)$$

and

$$
\begin{aligned}
V(S_C, \{\Lambda\}) &= \mathcal{V}(\{\Lambda\}) + V_1(S_1) \\
&= \mathcal{V}(\{\Lambda\}) + V_1\Big[S_C - \mathcal{S}(\{\Lambda\})\Big], \quad (2.6)
\end{aligned}
$$

where $\mathcal{S}(\{\Lambda\})$ is the entropy associated with the internal state variables; $\mathcal{V}(\{\Lambda\})$ is the corresponding volume; and S_1 and V_1 are, respectively, the entropy and volume associated with all the degrees of freedom other than the $\{\Lambda\}$. Then, for each α,

$$\frac{\partial V}{\partial \Lambda_\alpha} = \frac{\partial \mathcal{V}}{\partial \Lambda_\alpha} - X\,\frac{\partial \mathcal{S}}{\partial \Lambda_\alpha} = \frac{\partial}{\partial \Lambda_\alpha}\,\mathcal{F}(\{\Lambda\}), \qquad (2.7)$$

where

$$\mathcal{F}(\{\Lambda\}) = \mathcal{V}(\{\Lambda\}) - X\,\mathcal{S}(\{\Lambda\}). \qquad (2.8)$$

Inserting this result into Eq.(2.3), satisfying the second-law inequality separately for each term in the sum over α, and taking the equilibrium limit, we find that

$$\dot{\Lambda}_\alpha \propto -\frac{\partial}{\partial \Lambda_\alpha}\,\mathcal{F}(\{\Lambda\}) \to 0. \qquad (2.9)$$

Thus, $\mathcal{F}(\{\Lambda\})$ is a "free volume," analogous to a free energy, whose minimum in the space of variables $\{\Lambda\}$ locates the equilibrium state of the system. The values of the $\{\Lambda\}$ are determined by the equations

$$\frac{p}{\theta} = \frac{\partial \mathcal{S}/\partial \Lambda_\alpha}{\partial \mathcal{V}/\partial \Lambda_\alpha}. \qquad (2.10)$$

Note that Eq.(2.10) is what we would have found had we simply maximized the entropy $\mathcal{S}$ for a fixed volume $\mathcal{V}$, and used $X = \theta/p$ as a Lagrange multiplier. The preceding derivation is more general in the important sense that it includes the residual quantities S_1 and V_1, which will play a role in the following analysis.

III.   TWO-STATE SYSTEMS

The first step in constructing a model of hard-core particles within the framework outlined in Sec. II must be to choose the internal state variables Λ_α. In doing this, we must decide which of the degrees of freedom of the system as a whole are statistically relevant, and therefore should be included among the Λ_α, and which can be included implicitly in the residual quantities S_1 and V_1 defined in Eqs.(2.5) and (2.6).

In some way, one or more of these variables must describe the bond-orientational order observed by Tanaka et al..[1] Tanaka's principal innovation has been to look for spatial correlations, not between particle positions per se, but between the positions of particles in topologically similar environments. Specifically, in what I believe to be the most definitive of their two-dimensional simulations [1], Tanaka et al. measured the time-averaged, complex, hexatic order parameter $\bar{\Psi}_6$ as a function of position and packing fraction ϕ; and they computed the two-point correlation $\langle \bar{\Psi}_6(r)\,\bar{\Psi}_6^*(0)\rangle$ as a function of the separation r. From the latter quantity, they computed the correlation length $\xi(\phi)$, and found that it scaled as described in Sec. I as a function of $t \equiv (\phi_c - \phi)/\phi_c$, where the critical packing fraction ϕ_c has replaced T_c^{-1}. Similar results were obtained in three dimensions, where the relevant topological order parameter was found to be the degree of hexagonal-close-packed (as opposed to icosahedral) order. (See also [17].)

It might seem that a topological order parameter such as $\bar{\Psi}_6$ would necessarily be one of the Λ_α. Indeed, $\bar{\Psi}_6$ is frequently used as an argument of a Landau free energy, from which equilibrium states of two-dimensional systems are determined by a variational procedure formally identical to Eqs.(2.8) and (2.10). (For example, see [18].) However, we need to look more closely at such models before trying to use them to describe glass formation.

In the monodisperse limit, Tanaka's hard disks undoubtedly undergo the liquid-hexatic transition that has been studied intensely ever since the pioneering numerical simulations of Alder and Wainwright.[19] The standard description of such transitions in microscopically uniform materials is the two-dimensional melting theory of Kosterlitz, Thouless, Halperin, Nelson and Young [20–24]; but this "KTHNY" theory may not be what we need to describe the most important properties of polydisperse, glass-forming liquids. KTHNY describes the melting of an hexatically ordered phase as a process in which a dilute population of disclination pairs undergoes a thermally induced unbinding transition, thereby destroying long-range orientational order in a distinctly non-Ising manner. In contrast, a glass-forming liquid, well away from a KTHNY transition, cannot naturally be described by a population of disclinations. Even if it were possible to do so in some formal way, we know that the KTHNY analysis fails when that population becomes too dense, as must happen in the liquid phase. Thus, it should be more productive to construct a theory in which topological order emerges from within a liquidlike state, instead of, as in KTHNY, starting from a state with infinitely long range order and asking how it melts.

Accordingly, I propose that the fluctuating liquid state of a glass-forming material be visualized as one in which topologically ordered clusters of particles appear and disappear in a background of disordered, fluidlike particles. These ordered clusters may be favored by steric (or energetic) interactions; in the liquid phase, they are disfa-

vored by the entropy of the system as a whole. As the pressure is increased, they come closer together, and the steric forces make it favorable for them to be aligned with each other. Thus, topological order grows with pressure.

My main hypothesis is that these clusters are statistically most likely to be two-state systems. The glass literature contains many references to such systems. For example, in 1972, Anderson, Halperin and Varma [10] based their theory of low-temperature anomalies in glasses on the hypothesis that "in any glass system there should be a certain number of atoms (or groups of atoms) which can sit more or less equally well in two equilibrium positions." More recently, my colleagues and I have used a similar argument to justify the model of two-state, shear transformation zones (STZ's) that we have used in theories of amorphous plasticity.[11] Twofold symmetry is especially important for present purposes because it is the Ising symmetry, and thus is consistent with the observed Ising-like critical exponents. Moreover, the following argument in favor of twofold symmetry is independent of the specific nature of the ordering, or even the dimensionality, and thus may lead to the kind of universality that seems to be emerging in the computational experiments.

To see how two-state systems might naturally occur in theories of disordered materials, note that a spatially varying order parameter such as $\bar{\bar{\Psi}}_6$ should be defined as an average over some coarse graining length scale. If that scale is too small, say, only one or two particle spacings, then $\bar{\bar{\Psi}}_6$ will be large in some places and small in others; but changing the local orientation at an hexatic site, i.e. changing the phase of $\bar{\bar{\Psi}}_6$, almost certainly increases the local volume (or energy), so that the system is rigid at particle-sized length scales. At the other extreme, if the coarse-graining scale is very large, and if we are not too close to an orientational ordering transition, then many different orientations will be degenerate in the sense of having the same volumes or energies, but the averaged magnitude of $\bar{\bar{\Psi}}_6$ will be too small to provide useful information. I propose, therefore, that the natural coarse-graining scale – the one that provides the statistically most relevant information – is the one for which the ordered clusters are most likely to be twofold degenerate, simply because two is the smallest integer greater than one.

This coarse-graining argument immediately points to a limitation of the theory. As an Ising system approaches a critical point, the correlations become long ranged, and a renormalization-group analysis like that used by KTHNY requires that we coarse-grain on increasingly large length scales. For hard disks in two dimensions, we eventually restore circular ("xy") symmetry [21], and cross over into a regime where the KTHNY analysis again becomes valid. As a result, even for a polydisperse system, there must be a region near a critical ordering transition where the correlation length diverges according to the KTHNY prediction. This crossover region may be unobservably small as a function of packing fraction for large polydis-

persities; but I think it must be there in principle. Conversely, the crossover may also occur for a monodisperse system, because the liquid phase is intrinsically disordered away from criticality.

The fundamental question regarding the two-state hypothesis is whether it can be derived systematically from a well defined description of a many-body system. I see no reason why such a derivation should not be possible. Perhaps the many-body strategy presented recently by Yaida [25], which also concludes that glassy systems belong to the Ising universality class, is a step in this direction. However, in the next several Sections, I simply take the two-state model literally, and examine how its predictions compare with the simulation data.

IV. ISING-LIKE MODEL

A. Binary Clusters

To describe the two-state picture mathematically, let N_+ and N_- be extensive variables denoting the numbers of, say, "binary clusters" oriented in $+$ and $-$ directions with respect to some direction in space. Degeneracy requires that, when a cluster switches between $+$ and $-$ orientations, it continues to make the same contribution, say v^*, to the volume $\mathcal{V}$ introduced in Eq.(2.6). Just as in the STZ theory, the actual orientations denoted by $\pm$ need not be specified initially. In the STZ case, we usually interpret the $N_\pm$ to be the numbers of zones whose orientations are more nearly parallel or antiparallel to an applied stress. In contrast to the STZ's (or the disclinations), there is no reason why the population of binary clusters should be dilute. A large ordered region at high compression may consist almost entirely of aligned clusters, whose specific orientation may be the result of an accidental anisotropy or a spontaneously broken symmetry.

The way in which orientational order is propagated between neighboring positions in this model is via an Ising-like interaction, in which neighboring clusters make smaller contributions to the volume if their orientations are aligned than if they are opposite to each other. Another way of thinking about this is that the neighboring clusters break each other's orientational degeneracies in such a way as to increase the probability of their alignment. This steric effect, the analog of an Ising exchange coupling, is the reason why orientational order increases in response to increasing pressure.

To make direct comparisons with the functions $p(\phi)$, we need one more internal variable to describe how the system as a whole expands and contracts in response to changing pressure, and how that behavior couples to the internal state of topological order. For this purpose, it is useful to introduce a population of, say, N_0 "voids" occupying volumes v_0. In order to play a role comparable the the $N_\pm$, N_0 must be a collective variable describing a property of groups of particles comparable in size to

the binary clusters, and v_0 must be a volume associated with more than just one, particle-size void. With the extra degree of freedom described by N_0, the model can make a transition with increasing pressure from dilute, liquidlike states with large populations of voids, to dense ordered states in which the voids disappear. Tanaka et al. show such voids in their Voronoi tiling patterns for two dimensional systems (see Fig. 2 in [1]), and assert that these voids play a role in limiting the extent of hexatic correlations. That happens here as well.

B. Volume

In a first, mean-field statement of this model, the volume $\mathcal{V}$ defined in Eq.(2.6) is

$$\mathcal{V} \cong N^* v^* + N_0 v_0 - \frac{J}{2(N^* + N_0)}(N_+^2 + N_-^2), \quad (4.1)$$

where $N^* = N_+ + N_-$ is the total number of binary clusters, and is therefore proportional to the extensive number of statistically relevant, orientational degrees of freedom associated with the partial volume $\mathcal{V}$ and the partial entropy $\mathcal{S}$. The pairwise interaction, proportional to the "exchange coupling" J, is approximated here by the sum of the squares of the densities of the $\pm$ clusters.

To see the analogy between Eq.(4.1) and an Ising system, define

$$m = \frac{N_+ - N_-}{N^*}, \quad \eta = \frac{N^*}{N^* + N_0}. \quad (4.2)$$

The variable m is analogous to a magnetization; here, it is the bond-orientational order parameter. η is a measure of how close the system is to jamming; it vanishes in the dilute limit, $N_0 \to \infty$, and goes to unity at high density where the voids are squeezed out of the system. In terms of these variables, Eq.(4.1) becomes

$$\frac{\mathcal{V}(m, \eta)}{N^*} = v^* + \left(\frac{1}{\eta} - 1\right) v_0 - \frac{1}{4} J \eta (1 + m^2). \quad (4.3)$$

Note that the term proportional to J contains a factor η, implying that ordering becomes weaker with increased numbers of voids. Note also that $\mathcal{V}(m, \eta)$ is proportional to N^*. Because the partial entropy $\mathcal{S}$ also must be proportional to N^*, the latter quantity cancels out of the formula for the pressure, and there is no need to include it among the relevant internal variables. As a result, we can assume that $\{\Lambda\}$ consists of just the two variables m and η.

Equation (4.3) provides a formula for the packing fraction

$$\phi = N_{tot} \frac{\langle v \rangle}{V}, \quad (4.4)$$

where N_{tot} is the fixed total number of particles in the system, and $\langle v \rangle$ is the average volume of a single particle. If we measure all volumes, including J, in units such that

$$N_{tot} \langle v \rangle = N^*, \quad (4.5)$$

then we can write

$$\frac{1}{\phi} = \tilde{v} + \left(\frac{1}{\eta} - 1\right) v_0 - \frac{1}{4} J \eta (1 + m^2). \quad (4.6)$$

where $\tilde{v} = v^* + V_1/N^*$, and V_1 is the residual volume defined in Eq.(2.6). This scaling implies that both $\tilde{v}$ and v_0 are dimensionless numbers of the order of unity. The total number of particles contained in V_1 must be proportional to N_{tot}, i.e. $V_1 \sim N_{tot} \langle v \rangle$; and therefore, with the volume units defined in Eq.(4.5), $\tilde{v} \sim V_1/N^* \sim 1$. Similarly, the total volume associated with voids must scale like $N_0 v_0 \sim N_{tot} \langle v \rangle$. Since we have required N_0 to scale with N^* via Eq.(4.2), we again may use Eq.(4.5) to find that $v_0 \sim 1$.

C. Entropy

Much of the physics of this model is contained in the choice of the entropy $\mathcal{S}$, defined in Eq.(2.5). Like $\mathcal{V}$, $\mathcal{S}$ must be proportional to the number of statistically relevant degrees of freedom, N^*. Assume that $\mathcal{S}$ can be written in the form

$$\mathcal{S}(m, \eta) \cong \mathcal{S}_1(m) + \mathcal{S}_2(\eta). \quad (4.7)$$

The two-state model implies that $\mathcal{S}_1$ is an Ising-like function:

$$\frac{\mathcal{S}_1(m)}{N^*} = \ln(2) - \frac{1}{2}(1 + m)\ln(1 + m)$$
$$- \frac{1}{2}(1 - m)\ln(1 - m). \quad (4.8)$$

The choice of $\mathcal{S}_2$ is more interesting and problematic. If we make a lattice-gas approximation in which the N_0 voids are distributed randomly over $N^* + N_0$ sites, we find

$$\frac{\mathcal{S}_2(\eta)}{N^*} \approx -\ln(\eta) - \left(\frac{1}{\eta} - 1\right)\ln(1 - \eta), \quad (4.9)$$

which has an ideal gas limit as $\eta \to 0$, but vanishes very weakly as $\eta \to 1$. On the other hand, van der Waals behavior, with $p \sim \partial\mathcal{S}/\partial\eta \sim (1-\eta)^{-1}$, would require that $\mathcal{S}_2 \sim \ln(1 - \eta)$, which is unphysical because it diverges as $\eta \to 1$.

My proposed alternative is

$$\frac{\mathcal{S}_2(\eta)}{N^*} = -\ln(\eta) + \frac{A}{1 - \epsilon}(1 - \eta)^{1-\epsilon}, \quad (4.10)$$

where the parameter ϵ must be in the range $0 < \epsilon < 1$. Along with the adjustable parameter A, ϵ tunes the strength of the jamming behavior between weak and strong limits. For small ϵ, $\mathcal{S}_2$ approximates lattice gas behavior; as $\epsilon \to 1$, it resembles van der Waals. In any case, the choice of $\mathcal{S}_2$ for large η must be regarded as a phenomenological strategy for data fitting. We know

that this model lacks the ingredients for describing the way in which the system becomes jammed or crystalline at high densities. This is not a first-principles theory of such behavior; but it is useful to work with an approximate theory in which the jamming limit can be described.

D. Spatial Variations

A more general formulation of this theory starts with a partition function expressed as a functional integral over spatially varying values of m and η:

$$\mathcal{Z}(X) = \int \delta m \int \delta \eta \; e^{-\mathcal{F}(m,\eta)/X}. \qquad (4.11)$$

Relations such as Eq.(2.10) can be interpreted as mean-field results, obtained by making a saddle-point approximation in Eq.(4.11). As usual, write $\mathcal{F}/N^* \equiv f(m,\eta)$, and add a square-gradient term in the bond-orientational order parameter m:

$$\frac{\mathcal{F}}{N^*} \to f(m,\eta) + \frac{\xi_0^2}{2} \, (\nabla m)^2. \qquad (4.12)$$

Just as in the magnetic Ising model, the square-gradient term has its origins in the pairwise interactions proportional to J in Eq.(4.1).

The standard procedure [26] for dealing with critical systems of this kind is to start with the unrenormalized form of of $f(m,\eta)$, expand it in powers of m to obtain a Landau approximation, and then perform a renormalization-group analysis. Beyond m^4, the higher powers in the expansion become irrelevant; and it is easy to check that the fluctuations in η are non-critical. Thus, we know that this procedure produces the correct Ising scaling exponents for any set of starting parameters such that $f(m,\eta)$ has a mean-field critical point. Of course, this procedure tells us nothing about the possibility that the Ising symmetry might cross over to something else at large length scales.

V. EQUATIONS OF STATE

We already know from [1] and [8] that the correlation exponents for large enough polydispersities Δ are consistent with the renormalized Ising values $\nu \cong 2/d$. Thus, the most interesting comparisons now are for the equations of state, $p(\phi)$, for different Δ's, reported in [2].

The mean-field approximation using Eq.(2.10) means that we look for minima of $f(m,\eta)$ in the space of variables m and η. Thus, for variations with respect to m:

$$\frac{p}{\theta} = \frac{1}{J \, \eta \, m} \, \ln \left(\frac{1+m}{1-m} \right); \qquad (5.1)$$

and, for variations with respect to η:

$$\frac{p}{\theta} = \frac{1}{v_0 + (J/4) \, \eta^2 \, (1+m^2)} \left[\eta + \frac{A \, \eta^2}{(1-\eta)^\epsilon} \right]. \qquad (5.2)$$
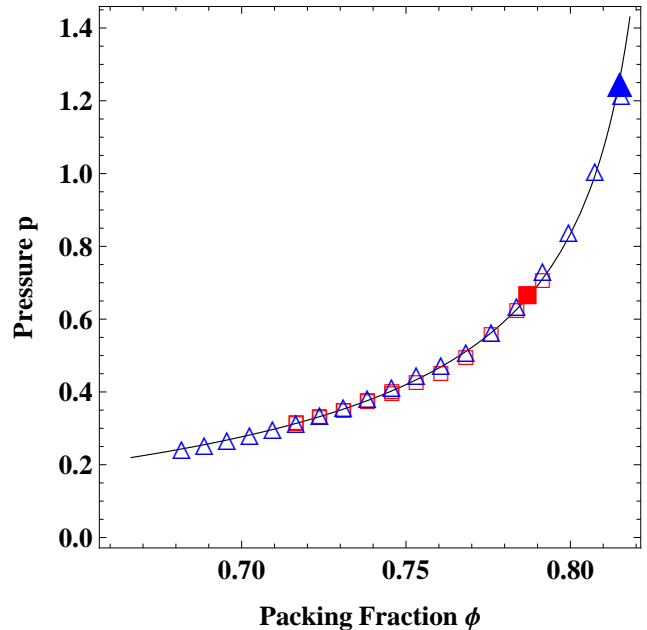

FIG. 1: (Color online) Pressure as a function of packing fraction for polydispersties $\Delta = 9\,\%$ (red open squares) and $13\,\%$ (blue open triangles). The critical points are indicated by the corresponding solid symbols. The blue theoretical curve shows the $J = 0$ limit according to Eqs.(5.3) and (5.4). The pressure is expressed in dimensionless units defined in [2].

The reference volume $\tilde{v}$ defined in Eq.(4.6), and the parameters v_0, A and J, should depend, at least in a first approximation, only on Δ, and not on η. With known values of these parameters, Eqs. (4.6), (5.1), and (5.2) can be solved for p/θ, m, and η as functions of ϕ.

Note that these equations recover a perfect gas law at very small values of η and $m = 0$. Eq.(5.2) implies that $p \approx \theta \, \eta/v_0$; and Eq.(4.6) implies that $\phi \approx \eta/v_0$. Thus, as expected, $p \approx \theta \, \phi$.

A second limiting behavior of these equations is especially interesting. Large polydispersities Δ are roughly equivalent to high temperatures, which, in the magnetic analogy, imply small values of the coupling coefficient J. Setting $J = 0$ in Eqs.(4.6) and (5.2), we find

$$\frac{1}{\phi} \to \tilde{v} + \left(\frac{1}{\eta} - 1 \right) v_0, \qquad (5.3)$$

and

$$\frac{p \, v_0}{\theta} \to \eta + \frac{A \, \eta^2}{(1-\eta)^\epsilon}. \qquad (5.4)$$

If the parameters $\tilde{v}$, v_0, A, and ϵ are independent of Δ in this limit, then the functions $p(\phi)$ should collapse onto a single curve. I show in Fig. 1 that this is nearly what happens for $\Delta = 9\,\%$ and $13\,\%$, the latter being the largest value for which I have data available. This limiting behavior provides a convenient way to fix several of the theoretical parameters.

The theoretical curve in Fig. 1 is computed from Eqs. (5.3) and (5.4) as follows. I arbitrarily have set $v_0 = 1$, in accord with the argument following Eq.(4.6). I also have set $\theta = 0.025$, which is the value given in [2], where it is measured in units of the strength of the truncated, repulsive, Lennard-Jones potential used in those simulations, and therefore sets the scale for the pressure p. The remaining parameters have been chosen to provide an accurate fit to the data – more accurate, I suspect, than is warranted by either the quality of the theory or the precision of the simulations. In this spirit, I find $\epsilon = 0.60$, about half way between the lattice gas and van der Waals limits, as discussed following Eq.(4.10). Like v_0 and θ, I assume that ϵ is a constant, independent of Δ. According to Eq.(5.3), the maximum packing fraction is $\phi_{max} = 1/\tilde{v}$. For this large-Δ limit, and this choice of ϵ, I find $\phi_{max} = 0.832$, and $A = 5.6$.

The Ising nature of Eqs.(4.6), (5.1) and (5.2) appears in their reflection symmetry under $m \to -m$, which is spontaneously broken at critical points. We can see this behavior at the mean-field level by expanding the logarithm in Eq.(5.1) to third order in m and solving the equation to find

$$m \approx \begin{cases} 0, & \text{for } \eta < \eta_c \\ \pm\sqrt{3(\eta/\eta_c - 1)}, & \text{for } \eta > \eta_c, \end{cases} \qquad (5.5)$$

where the critical value of η is

$$\eta_c = \frac{2\,\theta}{p_c\,J}, \qquad (5.6)$$

and p_c is the critical pressure. This "magnetization" formula changes substantially under renormalization; the mean-field exponent implied by the square root, $\beta = 1/2$, changes to $\beta = 1/8$ for $d = 2$ and $\beta \cong 0.325$ for $d = 3$. This abrupt increase in m for $\eta > \eta_c$ controls the behavior of the pressure at the onset of ordering *via* the quantity m^2 in the denominator of the right-hand side of Eq.(5.2). Any meaningful comparison of Eq.(5.2) with the data requires that we use an expression for m^2 that is consistent with the renormalized theory.

To approximate the renormalized behavior, I propose to replace the magnetization formula, Eq.(5.5), by one with the correct Ising exponent:

$$m \to M(\eta) = \begin{cases} 0, & \text{for } \eta < \eta_c \\ \mu\,[(\eta/\eta_c - 1)]^\beta, & \text{for } \eta > \eta_c, \end{cases} \qquad (5.7)$$

and to use this approximation in Eqs.(4.6) and (5.2) instead of the mean-field value of m determined by Eq.(5.1). In the absence of a simple, accurate interpolation from small to large values of $\eta/\eta_c - 1$, I have used Eq.(5.7) for all η, and have let μ be an adjustable parameter. The only vestige of Eq.(5.1) in the theory is the formula for η_c in Eq.(5.6), which is obtained from Eq.(5.1) by taking the limit $m \to +0$. We now may interpret p_c, ϕ_c, and η_c to be the renormalized values of those quantities; thus they are numbers that we can deduce directly from the data.
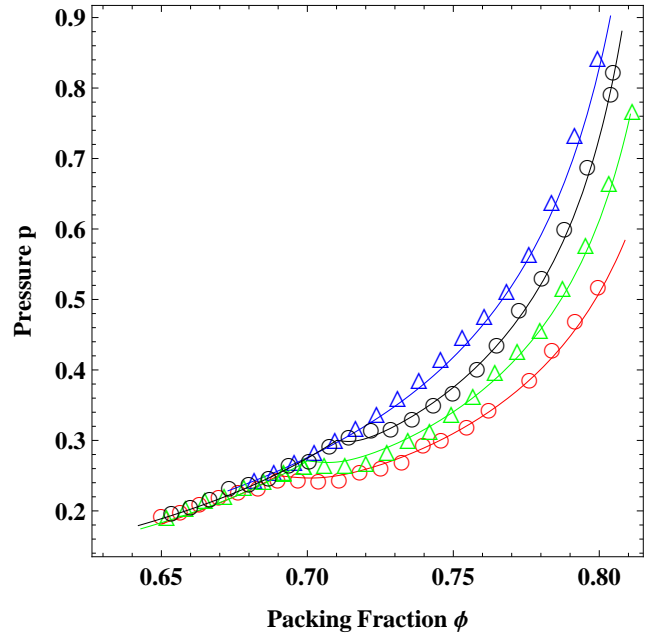

FIG. 2: (Color online) Pressure as a function of packing fraction, from bottom to top, for polydispersties $\Delta = 0\,\%$ (red circles), $5\,\%$ (green triangles), $7\,\%$ (black circles), and $13\,\%$ (blue triangles).

The results of these calculations, along with the simulation data from [2], are shown in Fig. 2 for selected polydispersities: $\Delta = 0\,\%$, $5\,\%$, $7\,\%$, and $13\,\%$. For $\Delta \leq 8\,\%$, the values of p_c and ϕ_c have been estimated directly from the data, because the cusp-like changes in slope at the critical points are visible. For larger Δ's, ϕ_c has been evaluated in [2] by fitting various relaxation-time measurements to a VFT formula; and the value of $\phi_c = 0.787$ for $\Delta = 9\,\%$ also is consistent with the correlation-length measurements reported in [1]. The critical points for $\Delta = 9\,\%$ and $13\,\%$ are indicated respectively by the solid square and the solid triangle in Fig. 1.

If we know p_c and ϕ_c for a given Δ, then Eqs.(4.6) and (5.2), evaluated at $m = 0$ and $\eta = \eta_c$, plus the definition of η_c in Eq.(5.6), provide three constraints on the five remaining unknown parameters: η_c, $\tilde{v}$, J, A, and μ. A fourth constraint is obtained by estimating ϕ_{max} by setting $\eta = 1$ in Eq.(4.6), but keeping nonzero J; that is

$$\frac{1}{\phi_{max}} \cong \tilde{v} - \frac{J}{4}\left[1 + M^2(1)\right]. \qquad (5.8)$$

This is an approximate relation, because $M(\eta)$ given by Eq.(5.7) is not accurate at $\eta = 1$; but Eq.(5.8) is a useful consistency check on the earlier large-Δ estimate, especially in view of our lack of information about the jammed or ordered states in this limit. The only remaining free parameter in this analysis is μ. In computing the theoretical curves shown in Fig.2, I have used μ as the primary fitting parameter, and have kept $\phi_{max} = 0.832$ for all Δ.

The comparisons between the theoretical curves and the data in Fig.2, and similar comparisons for other values of Δ not shown here, reveal physically plausible trends in the underlying parameters, especially the coupling coefficient J. The main trend is that the critical points shift to higher values of ϕ with increasing Δ, because increasing polydispersity suppresses the ordering transition. The theoretical mechanism that produces this effect is the decrease in J shown in Fig. 3. In accord with the observations of Tanaka and coworkers, J drops abruptly at about $\Delta = 8\,\%$; but it does not drop to zero. The values of J for $\Delta = 9\,\%$ and $13\,\%$ have been computed as above, but using values for ϕ_c obtained from the correlation length and relaxation time analyses instead of directly from the $p(\phi)$ curves. This procedure produces values of $\tilde{v}$ and A that are consistent with the $J = 0$ analysis, and does not visibly affect agreement with the data for $p(\phi)$; thus it serves as a self-consistency check. The small but nonzero values of J at large Δ produce Ising-like glass transitions.
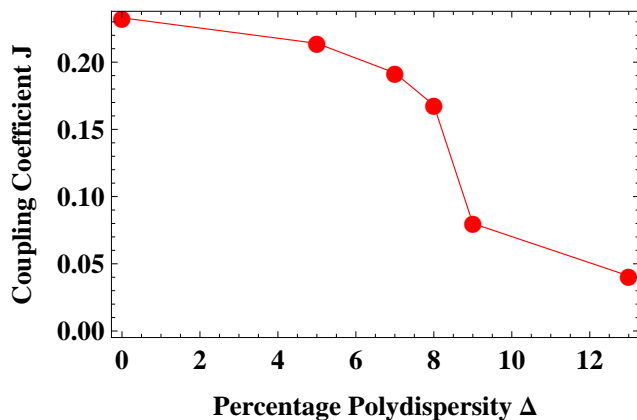

FIG. 3: (Color online) Dimensionless coupling coefficient J as a function of percentage polydispersity Δ

There are also more subtle effects. The reference volume $\tilde{v}$ should be a slowly decreasing function of Δ because, at large polydispersities, smaller particles can fit into the spaces between larger particles in ways that do not happen in monodisperse systems. The computed $\tilde{v}$ does decrease slightly from 1.33 at $\Delta = 0\,\%$ to 1.21 at $\Delta = 13\,\%$. The parameter A is a measure of the entropy and, accordingly, increases with "temperature" Δ in this region, from 4.0 to 5.6, the latter value being the same as the one deduced from the $J = 0$ analysis. The magnetization parameter μ decreases from 1.6 at $\Delta = 0\,\%$ to about 1.0 at $\Delta = 8\,\%$, but becomes impossible to measure at the larger Δ's where the critical transition is not visible in the $p(\phi)$ curves. In plotting the curves for $\Delta = 9\,\%$ and $13\,\%$, I have simply set $\mu = 0$.

VI. RELAXATION RATES

In [2], Kawasaki and Tanaka devote a sizable part of their effort to various measurements of the structural relaxation time τ_α, which they fit to a VFT function to determine critical packing fractions ϕ_c. They assume, as do I, that this ϕ_c is the same as the one that governs the diverging correlation lengths. The obvious question, then, is whether there is a sense in which the VFT formula is a manifestation of Ising-like symmetry. Here is one suggestion about how that may happen.

Assume that structural rearrangements in glassy materials near thermodynamic equilibrium are governed by the appearance, disappearance, and internal transitions of shear transformation zones (STZ's) [11, 27, 28]. The STZ's are localized, two-state, flow defects, which must contain excess volume (rather than energy) in these hard-core systems, and which can undergo shear transitions between their two states in the presence of thermal or mechanically generated noise. If the characteristic excess volume of an STZ is v_Z, then the equilibrium population of such defects is proportional to a Boltzmann factor $\exp(-v_Z/X)$, where $X = \theta/p$. To estimate a spontaneous formation rate, multiply this Boltzmann factor by an attempt frequency, $\rho(X)/\tau_0$, where τ_0 is a microscopic time determined by the kinetic energies of the particles or the thermal fluctuations of the fluid in which they are suspended. The dimensionless factor $\rho(X)$ describes glassy slowing down as X decreases.

Kawasaki and Tanaka [2] show by direct imaging that relaxation events occur primarily in disordered regions, consistent with the observation of Widmer-Cooper and Harrowell [30] that particles undergo rearrangements in regions of high "propensity." In the present picture, this observation means simply that the STZ formation volume v_Z is smaller in the disordered regions than in the ordered ones, so that the STZ's appear most frequently in the former. However, the attempt frequency $\rho(X)$ should be a property of the system as a whole, rather than being determined just by the local environments of a few particles. (See [28] for a discussion of the role of STZ's as dynamic heterogeneities and their relation to stretched-exponential relaxation.)

A scaling argument made in a different context by Kirkpatrick et al. [5] is useful for estimating a system dependent $\rho(X)$. Consider a correlated volume of size $\mathcal{V}_{corr} \sim \xi^d$. Near a critical glass transition, such a volume consists of a large number of particles individually making small, random displacements. Therefore, it undergoes Gaussian fluctuations of magnitude proportional to the square root of its size; that is, $\delta\mathcal{V}_{corr} \sim \xi^{d/2}$. The frequency of such fluctuations is proportional to

$$\rho(X) \sim e^{-\delta\mathcal{V}_{corr}/X} \sim e^{-\xi^{d/2}/X_c} \sim e^{-1/t^w}, \qquad (6.1)$$

where hyperscaling tells us that $w = d\nu/2 = 1 - \alpha/2 \cong 1$ for both $d = 2$ and 3. (Here, α denotes the specific heat exponent, which is known to be small.) Thus, we recover the VFT formula.

We can push this argument a bit further by noting that it implies

$$\log\left(\frac{\tau_\alpha}{\tau_0}\right) \approx \frac{D\,\phi}{\phi_c - \phi}; \quad D = p_c\,(a\,\xi_0)^{d/2}/\theta, \qquad (6.2)$$

where a is the linear size of a particle. The bare correlation length ξ_0, defined in Eq.(4.12), may be approximately the linear size of a binary cluster, and therefore ought to be a small multiple of a. We know that p_c increases with Δ. Thus, the "fragility" parameter D is predicted to increase with Δ – the glass becomes "stronger" – in at least qualitative agreement with the increasing values of D shown in the inset to Fig. 7 of [2].

I find the argument leading to Eq.(6.1) to be too simple, especially in view of the fact that the VFT formula has not proved to be an accurate representation for wide ranges of experimental data. In recent applications of STZ theory [13, 29], my coworkers and I have found it better to determine $\rho(X)$ from simulation data than to try to predict it theoretically. Nevertheless, this argument may provide yet another element of support for the Ising model of glassy behavior. Perhaps the limitations of this model, to be summarized briefly in Sec. VII, also will help us understand the limitations of the VFT formula.

VII.   CONCLUDING REMARKS

My main hypothesis is that the orientational bias of a population of twofold-degenerate "binary clusters" is the statistically relevant internal state variable that describes a broad class of disordered systems in which the constituent particles have a tendency to develop topological order. If and when this hypothesis is correct, the system exhibits Ising-like behavior; in particular, correlation lengths associated with the favored topology appear to diverge with Ising-like critical exponents. These Ising correlations have been observed in several numerical simulations, primarlily by Tanaka and coworkers. As suggested in Sec. VI, the observed Vogel-Fulcher-Tamann behavior of structural relaxation times may also be evidence in favor of the two-state hypothesis.

Tanaka's sequence of two-dimensional, hard-disk transitions, visible in the functions $p(\phi)$ shown here in Fig. 2, indicates a crossover from hexatic to glassy transitions with increasing polydispersity Δ. As discussed at the end of Sec. III, however, we know that the theory is wrong in the close vicinity of these critical points, because the Ising symmetry must change to full circular symmetry when the correlations become sufficiently long ranged. We know from numerical studies by Jaster [31] that the monodisperse hard-disk system undergoes a KTHNY transition with a correlation length that grows exponentially near ϕ_c, in contrast to the power-law growth char-

acteristic of Ising systems. We also know from Anderson et al. [32] that, when examined numerically with high precision extremely close to ϕ_c, this transition is revealed to be weakly first order. There is also an experimental study by Han et al. [33], who see KTHNY behavior for two-dimensional colloids at 3 % polydispersity.

When looked at somewhat less closely, however, the two-state Ising theory appears to be remarkably successful. It correctly predicts a sequence of critical ordering transitions with diverging correlation lengths, even for $\Delta = 0$. The arguments in Sec. III, if correct, make the Ising symmetry seem robust; there is no place in the two-state picture for a symmetry-breaking analog of a magnetic field. The theory also makes roughly credible predictions for the ordered states at $\phi > \phi_c$, where the correlations again become short ranged, and mean-field approximations may regain validity. The small, negative values of $dp/d\phi$ in the transition regions might be physically realistic indications of the weak, phase-separation instability reported in [32].

The conjectured validity of mean-field approximations in the ordered regime might make it possible for some missing ingredients of the theory to be restored within the Ising-like formulation. For example, the theory in its present state contains no hint of translational order. It does not tell us how or where to look for competition between glass formation and crystal growth. It resorts to a phenomenological expression for the entropy, in Eq.(4.10), for computing the pressure at high packing fractions, where translational order should be present, at least for small Δ. It says nothing specific about the orientations of the local topologies, or the possibility of "grain boundaries" between topologically oriented regions. It contains no information about how particles of different sizes are distributed spatially. For example, in a bidisperse system of hard disks, Donev et al. [34] found phase separation between the large and small particles in quilibrated structures at the highest densities. If the two-state, Ising-like model does provide a reasonable starting approximation, then it might accomodate some of these other physical properties of glassy materials.

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